

## PATENT SPECIFICATION

DRAWINGS ATTACHED

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## COMPLETE SPECIFICATION

## Improvements in or relating to the production of Metal Coatings

We, SIEMENS AKTIENGESELLSCHAFT, a German Company, of Berlin and Munich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of metal coatings and, more particularly, is concerned with a process for the deposition of a metal *A* from a reducing bath on to a body *B* comprising a semiconductor or a metal more noble than the metal *A*.

It is known to deposit a metal *A* on to a metal body *B* from a bath by reduction. If the metal *B* is more noble than the metal *A*, the surface of the metal body *B* must be seeded with a metal *C* which is equally noble or less noble than the metal *A* which is to be deposited. In order to achieve such seeding heretofore, the body consisting of the metal *B* has been suspended in the bath in baskets consisting of the metal *C* or from hooks consisting of the metal *C*, or it has been contacted with a piece of the metal *C* before it is introduced into the bath. These known methods have the disadvantage that a relatively long time is required for the deposition of the metal *A* and that with bodies having complex shapes, for example with pipes, no uniform metal coating is obtained inside said bodies. In addition, it has not been possible by means of the known processes described above to produce useful metal coatings on semiconductor bodies, since the bonding strength of the metal coatings on the semiconductor bodies has been insufficient.

According to the present invention there is provided a process for the deposition of a metal *A* from a reducing bath on to a body *B* comprising a semiconductor or a metal more noble than the metal *A*, wherein the surface of the body *B* is seeded with a metal *C* which is equally noble or less noble than the metal *A*

by suspending in the reducing bath particles of the metal *C*.

Advantageously, the metal *C* is suspended in the reducing bath by stirring or by heating the bath to its boiling point.

The time required for the deposition of metal *A* on to the body *B* is shortened to a quarter as compared with the known processes. Moreover, the process of the invention enables a uniform, firmly adhering metal layer to be deposited on complicated metal shapes and on semiconductor bodies.

For a better understanding of the invention, and to show how the same may be carried into effect, embodiments of the invention will now be described in the following Examples. In the Examples, which are concerned with the manufacture of thermocouple element legs from semiconductor material for example bismuth telluride, bismuth selenide or bismuth antimonides in the form of wafers, reference is made to the accompanying drawing in which:—

Figure 1 shows diagrammatically a bath 1 containing a stirrer motor 2 and holding means 3 for semiconductor wafers;

Figure 2 is a plan view of a semiconductor wafer 4 in the form of a disc provided with score lines 8, the score lines being used to divide the wafer into thermocouple element legs; and

Figure 3 is a section through a thermocouple element leg 5 which is provided with metal coatings 6 arranged on two opposite surfaces of the leg and with a second metal coating 7 which covers all surfaces of the thermocouple element leg.

## EXAMPLE 1

Semiconductor wafers 4 in the form of discs were treated for cleansing and surface enlargement with jets of sand having a grain size of  $10.10^{-3}$  to  $30.10^{-3}$  mm. The wafers were then boiled in methanol for 5 minutes at 70°C.

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and rinsed for another 5 minutes in methanol at 25°C. Thereafter, they were introduced into

either of two reducing baths having the following composition:

Constituent	1	2
	Concentration in g/l	
Nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	30	45
Sodium hypophosphite $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	10	11
Sodium citrate $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 4\text{H}_2\text{O}$	—	100
Ammonium chloride $\text{NH}_4\text{Cl}$	50	50
pH value	8—10	8—10
Temperature in °C.	90—99	90—99

- 10 1 g. per litre of aluminium powder having a grain size of  $15 \cdot 10^{-3}$  mm was suspended in the bath. The bath was heated to boiling point, and after 15 minutes a nickel layer with a thickness of  $3 \cdot 10^{-3}$  mm was deposited on the semiconductor wafers. After terminating the deposition, the wafers were rinsed in running tap water. Thereafter, they were again boiled for 5 minutes in methanol and rinsed in methanol at room temperature for 5 minutes. After cleaning, the coated wafers were dried and heat-treated for about 20 hours at 120°C. Thermocouple element legs 5 were then cut out of the semiconductor discs and thereafter provided with a second nickel layer 7 of

1.  $10^{-3}$  mm thickness by the method described above. The effect of this second nickel coating was that when forming the contacts, the edges of the leg of the thermocouple element were also well wetted with solder.

#### EXAMPLE 2

In order to produce legs of thermocouple elements with a cobalt-nickel alloy coating from semiconductor wafers, the semiconductor wafers were pretreated and after-treated as described in Example 1. A solution with the following composition was used as the reducing bath:

Constituent	Concentration in g/l
Cobalt chloride $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	30
Nickle chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	30
Sodium glycolate $\text{NaC}_2\text{H}_3\text{O}_3$	100
Sodium hypophosphite $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	20
pH value	5.0
Temperature in °C.	90—99

- 35 Once again 1 g per litre of aluminium powder having a grain size of  $15 \cdot 10^{-3}$  mm was suspended in the bath. The data for the duration of the deposition operation and the layer thickness of the resulting cobalt-nickel coating were the same as the corresponding data given in Example 1.

#### WHAT WE CLAIM IS:—

1. A process for the deposition of a metal A from a reducing bath on to a body B comprising a semiconductor or a metal more noble than the metal A, wherein the surface of the body B is seeded with a metal C which is equally noble or less noble than the metal A by sus-

- pending in the reducing bath particles of the metal C. 25
2. A process according to Claim 1, wherein the particles of metal C are suspending in the reducing bath by stirring the bath or by heating the bath to its boiling point. 25
- 5 3. A process according to Claim 1 or 2, wherein metal A is nickel. 30
4. A process according to Claim 1 or 2, wherein metal A is a cobalt-nickel alloy. 30
- 10 5. A process according to Claim 1, 2, 3, or 4, wherein the metal C, used to seed the surface of the body B, is aluminium powder. 35
6. A process according to Claim 5, wherein the aluminium powder has a grain size of about  $15.10^{-3}$ mm. 40
- 15 7. A process according to any one of Claims 1 to 6, wherein the body B comprises a semiconductor wafer.
- 20 8. A process according to Claim 7, wherein the process is carried out for a time sufficient to produce a coating of metal A on the body B having a thickness of about  $3.10^{-3}$ mm.
9. A process according to Claim 7 or 8, wherein the coated semiconductor wafer is divided into a plurality of pieces to form legs of thermocouple elements, and wherein the process is repeated so as to provide the legs with a second coating of metal A.
10. A process according to Claim 9, wherein said repeated process is carried out for a time sufficient to produce a second coating having a thickness of about  $1.10^{-3}$ mm.
11. A process according to Claim 1, substantially as hereinbefore described with reference to the foregoing Examples and to the accompanying drawing.
12. A coated body whenever produced by the process claimed in any one of the preceding claims.

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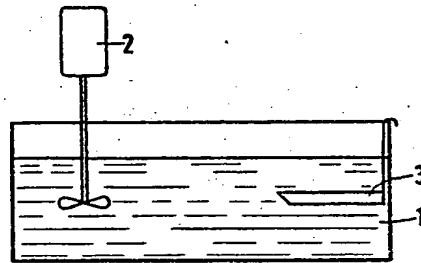


Fig. 1

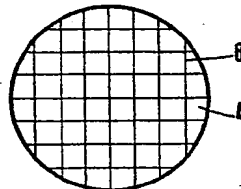


Fig. 2

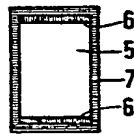


Fig. 3